Whole rock geochemistry and hyperspectral mineralogy of Western Australian LCT pegmatites

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SUMMARY

CSIRO Mineral Resources evaluates geochemical and optical sensing technologies for cost-effective exploration and ore body characterisation of a wide range of critical metals deposits, such as pegmatite-hosted Li-deposits. This paper presents varieties of ore and gangue mineral assemblages of five drill cores from the Greenbushes, King Col and Londonderry LCT pegmatites, located in the Yilgarn and Pilbara Cratons of Western Australia, respectively. The mineralogical drill core data were collected by the Geological Survey of Western Australia (GSWA) using a hyperspectral drill core scanner, HyLogger3, which is part of AuScope's National Virtual Core Library research infrastructure program. The HyLogger3 data are publicly available through the AuScope portal (http://portal.auscope.org.au/) and GSWA's GeoView portal (GeoVIEW.WA).

The thermal infrared hyperspectral data collected by HyLogger3 allow cost-effective mapping of Li-host minerals, such as spodumene, petalite, holmquistite and amblygonite. Spodumene represents the main Li-host at Greenbushes, whereas considerable amounts of petalite can be found at King Col in addition to spodumene. Holmquistite and amblygonite are minor Li-host minerals. A range of spectral signatures of spodumene and petalite can be observed in both mineral deposits and are potentially due to variations of chemical composition of the Li-host minerals, including Fe:Al and Li:Na ratios. Feldspars are common gangue minerals in both deposits and show different Na:Ca ratios down hole, indicating zoning of the ore body. The HyLogger3 data were used to identify 101 samples from Greenbushes drill core C3DD024 for FTIR and geochemical analysis, which allowed calibration of the HyLogger3 data and Partial Least Squares-modelling based prediction of Li, Na and other key geochemical elements across the five drill cores. Our case study demonstrates the potential for advanced but cost-effective Li-resource characterisation by means of reflectance spectroscopy, helping to assess the economic value of different ore bodies quickly.

Key words: lithium, spodumene, petalite, hyperspectral, thermal infrared.

INTRODUCTION

Lithium is critical for enabling the transition from a fossil fuel-based energy sector to a sustainable, renewable energy future. However, whereas Lithium demand could reach 2.8M t in 2028, mining capacity is only expected to reach about 2M t that year (Gallucci, 2021). The deficit in lithium supply will widen to 1.1 million tons by 2030 and recycling will potentially stay a small factor (Kramer, 2021), increasing exploration efforts for Li. The two main Li sources are LCT pegmatites and salt lakes. Most of the global Li production is from hard rock deposits whereas most of the world wide reserves are in salt lakes (USGS, 2019).

The Li rush has highlighted a lack of our understanding of pegmatite-hosted hard rock Li deposits with regards to the broad spectrum of Li-host minerals. Pure, unaltered spodumene contains the highest amount of Li and is amiable to current processing techniques. For example, spodumene at the Greenbushes Li deposit contains about 3.9 % Li_2O, from which a high-quality product of minimum 6 % Li_2O and maximum Fe_2O_3 is derived. However, the grade depends on the degree of alteration of spodumene (e.g. into minerals such as mica and chlorite) as well as whether Li is present in other potential Li-host minerals that are more difficult to process than spodumene (e.g. petalite, amblygonite, holmquistite). Furthermore, flotation is used to separate the denser spodumene from the lighter feldspar and quartz. However, flotation doesn't separate altered spodumene (into white mica and chlorite) from high-quality (i.e. less altered spodumene), which can lead to deleterious elements in the Li product. The complexity of Li-host and gangue minerals is usually poorly understood - especially during green-fields exploration – with significant impact on the economic viability of hardrock Li deposits. Understanding the mineral chemistry of Li-pegmatites as early as possible in the exploration stage could help avoiding investment in uneconomic resources and focussing on high quality Li deposits that can be exploited at a comparable low carbon footprint.

Reflectance spectroscopy has the potential for cost-effective characterisation of Li-host and gangue minerals, providing the mineral resources sector with critical information about the economic viability of mining hard rock Li occurrences. To evaluate the potential use of reflectance spectroscopy for this, publicly available HyLogger3 data from three

different Western Australian LCT-pegmatite systems – Greenbushes, King Col and Londonderry - were first compared with associated publicly available whole rock geochemistry and spectral reference library samples (https://mineralspectrallibraries.csiro.au/) made accessible as part of the AuScope National Virtual Core Library (NVCL) infrastructure program (https://www.auscope.org.au/nvcl). Furthermore, 101 samples from Greenbushes drill core C3DD024 were identified for further FTIR and geochemical analysis by using HyLogger3 data (Stromberg et al., 2021), which allowed calibration of the HyLogger3 data and Partial Least Squares-modelling based prediction of Li, Na and other key geochemical elements. Interpretation of the reflectance spectra and their comparison with whole rock geochemical analyses, as well as PLS modelling was completed in CSIRO's The Spectral Geologist (TSG) software.

All three discussed Western Australian LCT-pegmatite systems – Greenbushes, King Col and Londonderry - belong to the group of LCT pegmatites. A database about Western Australian rare element pegmatites is accessible from the Geological Survey of Western Australia (Duuring et al., 2020). LCT family pegmatites contain significant amounts of eponymous Li, Cs and Ta, but can also be enriched in Rb, Be, Sn, B, P and F (Cerny & Ercit, 2005). The other major group of pegmatites belongs to the NYF family, which is characterised by elevated amounts of Nb, Y and F in addition to Be, REE, Sc, Ti, Zr, Th and U. Derived from S-type and/or I-type granites, LCT pegmatites have a peraluminous character. Source rocks of LCT pegmatites comprise more specifically undepleted upper- to middle-crust supracrustal rocks and basement gneisses.

ANALYTICAL METHODS

HyLogger3

Drill core hyperspectral data of drill cores from Greenbushes, King Col and Londonderry were collected by the Geological Survey of Western Australia using a HyLogger-3, which records reflectance spectra in the visible-near (VNIR: 390 to 1000 nm), shortwave (SWIR: 1000 to 2500 nm) and thermal infrared (TIR: 6000 to 14500 nm) wavelength regions of the electromagnetic spectrum (Schodlok et al. 2016). The HyLogger-3 uses a computer-controlled X-Y table moving in a serpentine path under a fixed spectrometer and illumination system to log contiguous reflectance spectra in the VNIR, SWIR and TIR along samples, typically held in drill core or chip trays.

FTIR

TIR reflectance spectra were collected of 101 samples from drill core C3DD024 (Greenbushes, Western Australia) using a Fourier-transform infrared spectrometer (FTIR) coupled to an integrating hemisphere.

Whole rock geochemistry

Lithogeochemical analysis of 101 samples by ALS Laboratories (Perth) comprised full major element oxide analysis by XRF (ALS method ME_XRF26) and Li and B analysis by ICP-AES using 4 acid digest procedures (ALS method ME-ICP82b). The table below lists the analytical method for each element, unit of measurement, and lower level of detection.

RESULTS

TIR reflectance spectra of Li-bearing minerals

The VNIR-SWIR wavelength range reflectance spectra of Li-pegmatite mineral assemblages have been described earlier (e.g. Booysen et al., 2022; Cardoso-Fernandes et al., 2021; Mueller et al., 2022). However, the economically most significant Li-bearing minerals, such as spodumene and petalite, as well as key gangue minerals (e.g. quartz and feldspar), are not VNIR-SWIR active (Table 1). Minerals belonging to the group of nominally anhydrous silicates and phosphates display diagnostic spectral signatures in the TIR (Laukamp et al., 2021). TIR spectral signatures of pyroxenes, such as spodumene, were described by Hamilton (2000). The TIR spectral signatures of other major gangue minerals, such as quartz and feldspars, have been described elsewhere, but not for important Li-bearing minerals, such as petalite, holmquistite and amblygonite.

Figure 1 shows TIR reflectance spectra of Li-bearing minerals and gangue minerals common to LCT pegmatites. All silicates and phosphates produce primary reststrahlen bands in the 8000 to 12000 nm wavelength range. The 8000 to 10500 nm wavelength range shows significant overlaps between reststrahlen features of the spodumene and gangue minerals. However, the 10500 to 12000 nm wavelength region is less impacted by spectral signatures of gangue minerals, resulting in a characteristic spectral signature of spodumene-bearing samples in this wavelength range. The broad reflectance peak centred at around 10750 nm can be attributed to closely spaced fundamental Si-O stretching

vibrations in spodumene. Laukamp et al. (2022) discussed a potential shift of the wavelength position of the 10750 nm reflectance peak (and the neighbouring troughs) to shorter wavelengths that could potentially be used for estimating the Fe-content in spodumene by means of hyperspectral TIR field or drill core reflectance spectrometers. … …

Mineral	*Formula (IMA)*	*Theoretical Li content [%]*	*VNIR-SWIR*	*TIR*
Amblygonite	$LiAl(PO4)F$	3.4 – 4.7		x
Elbaite	$Na(Al_{1.5}Li_{1.5})Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)$	~1.11	x	x
Eucryptite	$LiAlSiO_4$	2.1 - 5.53		x
Hectorite	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2 \cdot nH_2O$	0.54 - 1.93	x	x
(Ferro-) holmquistite	$\square Li_2(Fe^{2+}_3Al_2)Si_8O_{22}(OH)_2$	~1.61	x	x
Lepidolite	$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$	1.39 – 3.6	x	x
Lithiophilite	$LiMn^{2+}(PO_4)$	~4.43		x
Montebrasite	$LiAl(PO_4)(OH)$	1 to 4		x
Petalite	$LiAlSi_4O_{10}$	1.6 – 2.27		x
Polylithionite	$KLi_2AlSi_4O_{10}F_2$	~3	x	x
Spodumene	$LiAlSi_2O_6$	~3.73		x
Zinnwaldite	$K(Al,Fe,Li)_3(Si,Al)_4O_{10}(OH)F$	~1.59	x	x

Table 1. Li-bearing minerals typically found in LCT-pegmatites and their theoretical Li-content. Columns "VNIR-SWIR" and "TIR" state which mineral is active in the respective wavelength ranges and shows diagnostic spectral signatures.
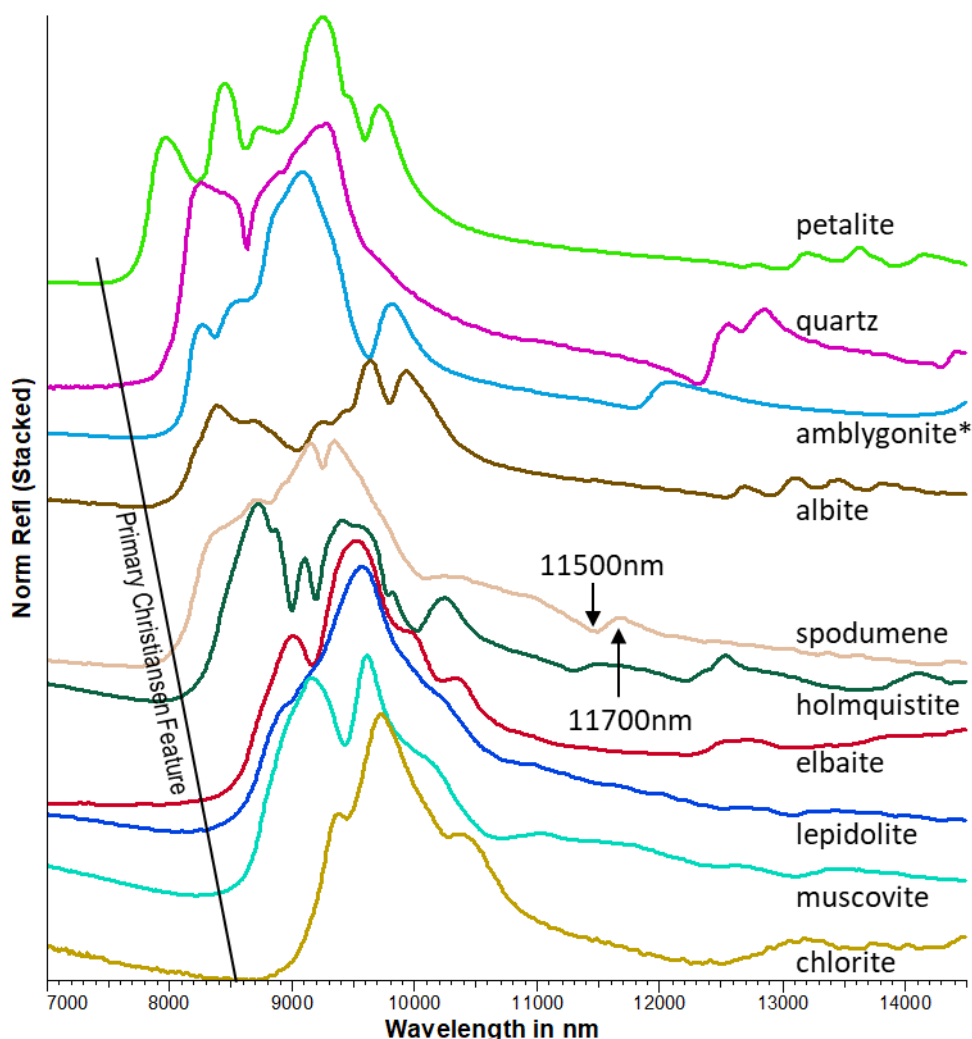
Figure 1. **Normalised (stacked) TIR reflectance spectra of Li-host and common LCT-pegmatite gangue minerals, sorted according to the wavelength position of the Primary Christiansen Feature (https://mineralspectrallibraries.csiro.au/home). All shown minerals (apart from amblygonite marked by *) are silicates, where the primary reststrahlen peaks are due to νT-O (T = Si, Al).**

HyLogger3 reflectance spectra and whole rock geochemistry of Greenbushes drill core C3DD024

Whole rock geochemistry provided by the GSWA for Greenbushes drill core C3DD024 can be used to subdivide two main zones, represented by the hanging wall Li-zone and footwall Na-zone (Figure 2a, b). The relative abundance of spodumene can be estimated by measuring the intensity of the diagnostic spodumene-feature centred at 11500 nm (Figure 1). Figure 2c shows a high correlation between the spodumene-rich intervals and the $Li_2O\%$ (Figure 2c). The relative abundance of Al-sheetsilicates (i.e. white mica and Al-smectite) can be estimated by measuring the relative intensity of Al-OH-related absorption features in the SWIR. A comparison of that relative abundance of white mica and/or Al-smectite and the wavelength position of the major Al-OH-related absorption at around 2200 nm highlights distinct intervals in the Li and the Na-zone, where the pegmatite mineral assemblage has been affected by considerable degrees of alteration and deformation (Figure 2d).
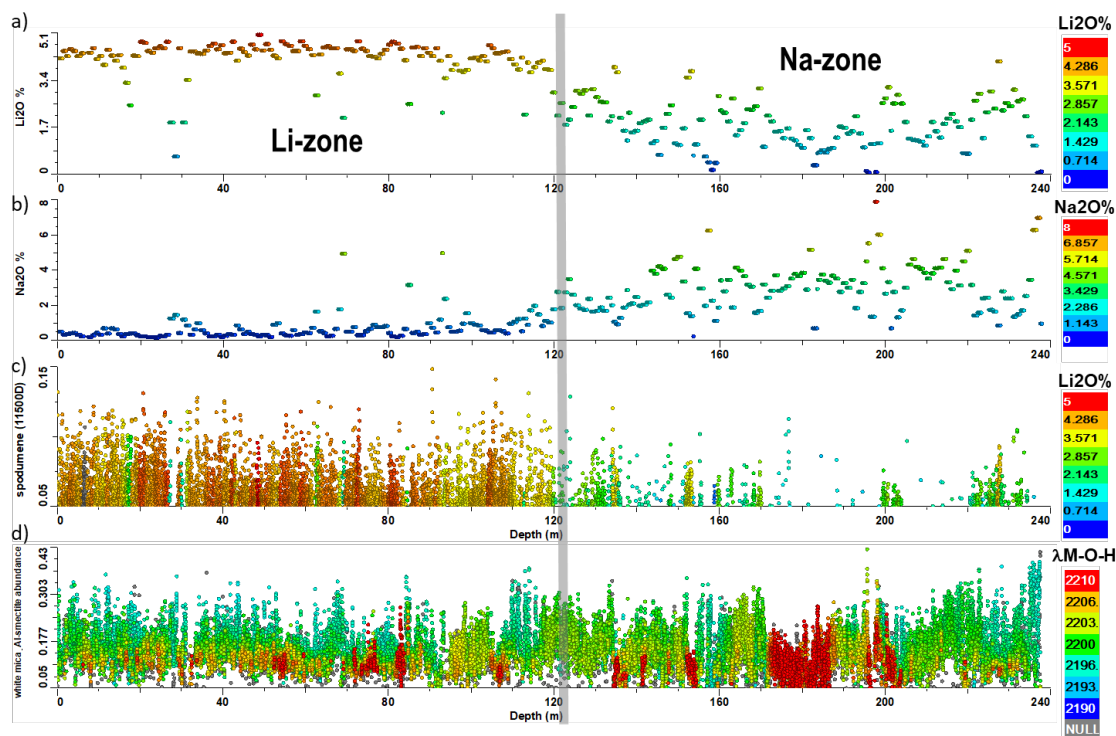
Figure 2. **Downhole plots (x-axis) of whole geochemical and mineralogical parameters for drill core C3DD024 (Greenbushes, WA). (a) Li₂O weight% (y-axis), coloured by same parameter; (b) Na₂O weight% (y-axis), coloured by same parameter; (c) Relative abundance of spodumene ("11500D", y-axis), coloured by Li₂O weight%; and (d) Relative abundance of white mica and Al-smectites (y-axis), coloured by the wavelength position of the major Al-OH-related absorption in Al-sheetsilicates centred at around 2200 nm.**

Comparison of HyLogger3-derived mineralogy

A comparison of HyLogger3-derived mineralogy for publicly accessible drill cores from Greenbushes, King Col and Londonderry are shown in Figure 3.
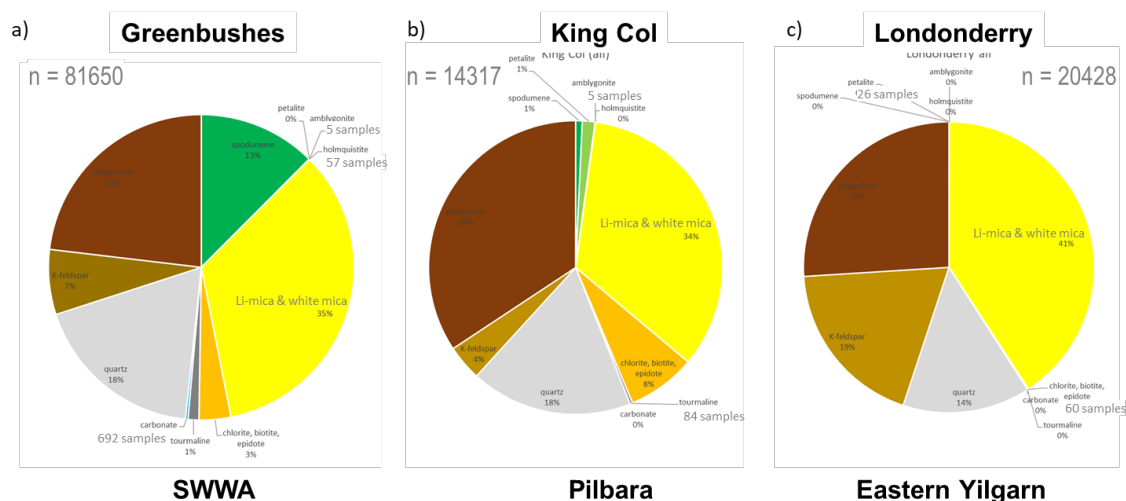

Figure 3. HyLogger3-derived mineral assemblages for (a) Greenbushes, (b) King Col and (c) Londonderry.

PLS-based modelling of geochemical parameters

Partial Least Squares (PLS) Regression is a statistical technique that models several dependant variables (Y) through a number of predictor variables (X) by relating two data matrices by a linear multivariate model (Wold et al., 2001). The

precision of the technique increases with the number of variables and observations and is, therefore, well-suited to matching geochemistry (Y) with spectral data (X), while being relatively insensitive to noise. In geoscience, PLS modelling approach has been applied mainly to hyperspectral reflectance spectra to predict modal mineral abundance (e.g. Laukamp et al., 2022). However, other case studies have successfully demonstrated the potential for PLS-based modelling of geochemistry, such as total organic carbon (Chang et al., 2005) and even elements in a polymetallic sulphide deposit (Desta et al., 2021), from hyperspectral data.

Figure 4 shows examples of a PLS-based prediction of Na% and Li% using 101 samples from the Greenbushes drill core C3DD024. PLS-modelling results are clearly better when the whole rock geochemistry is used to calibrate reflectance spectra collected from pulp samples (Figure 4a and c). However, even though the RMSE associated with predicting whole rock geochemistry in drill core samples (Figure 4b and d) is comparably high (i.e. 0.305 for Na and 0.914 for Li), the modelling results can be improved when excluding, for example, the modelling results for very low geochemical values (e.g. <1%Na).
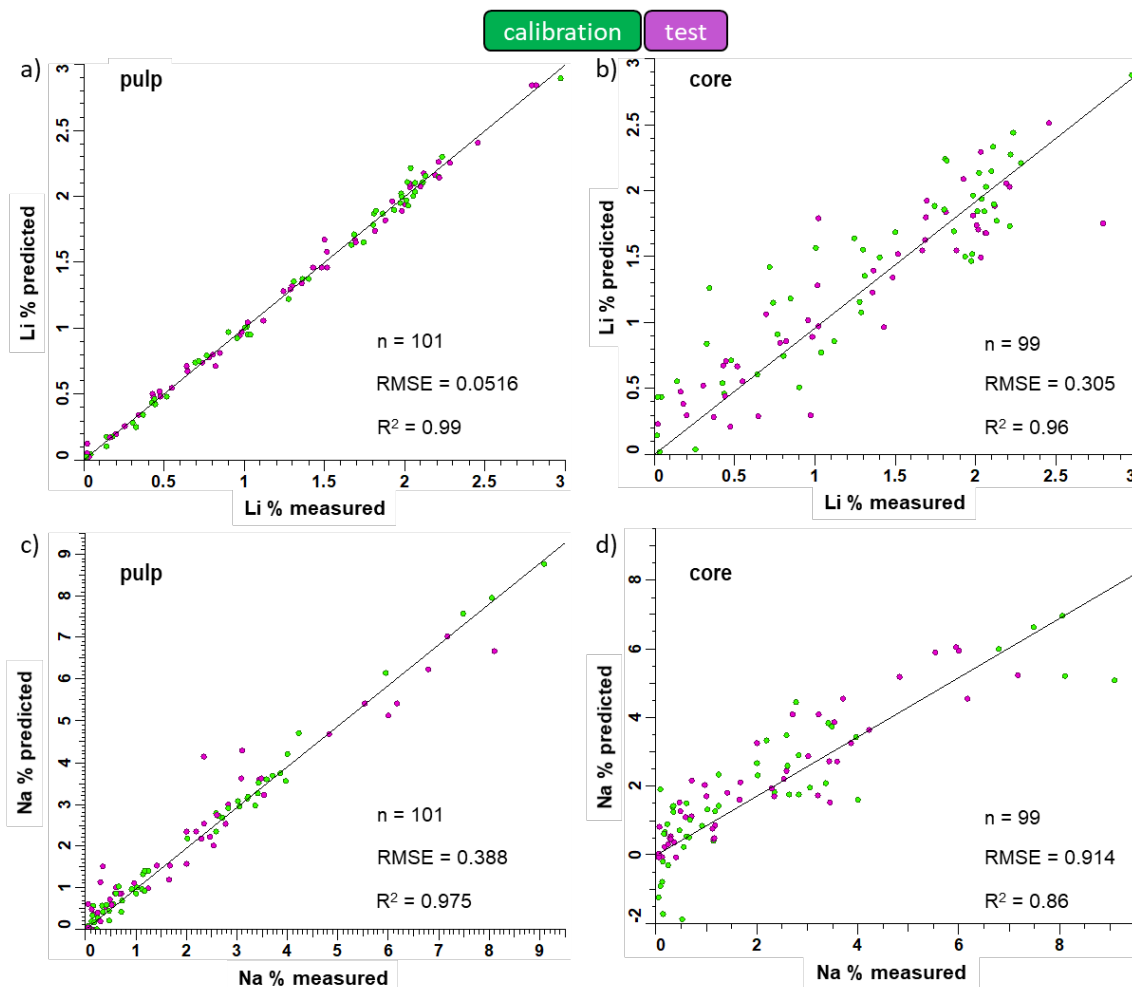

Figure 4. PLS models of Li and Na using 101 drill core samples from drill core C3DD024 (Greenbushes, Western Australia). (a) and (b) Comparison of measured Li % (x-axis) and predicted Li % using FTIR reflectance spectra collected from pulp and core samples, respectively. (c) and (d) Comparison of measured Na % (x-axis) and predicted Na % using FTIR reflectance spectra collected from pulp and core samples, respectively. All plots coloured by calibration (green) and test (purple) classification.

CONCLUSIONS

Thermal infrared hyperspectral data collected by HyLogger3 allow cost-effective mapping of Li-host minerals, such as spodumene, petalite, holmquistite and amblygonite. Spodumene represents the main Li-host at Greenbushes, whereas considerable amounts of petalite can be found at King Col in addition to spodumene. Holmquistite and amblygonite are minor Li-host minerals. A range of spectral signatures of spodumene and petalite can be observed in both mineral deposits and are potentially due to variations of chemical composition of the Li-host minerals, including Fe:Al and

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